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Single Sample Spin Generator Spectrometer

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Resonance conditions in the high-resolution nuclear magnetic resonance spectrometer are stabilized by a self-excited electronic circuit, frequency of oscillation being controlled by one of the lines of the sample under study. A very small width of this control line increases considerably the precision with which frequency follows the unstable field. Changes in the magnet's field configuration do not influence the results of the chemical shift measurements because both for the stabilization and recording of the spectrum the same sample is used.

1. High-resolution nuclear magnetic resonance requires both high magnetic field homogeneity and precise control of the magnetic field strength-frequency relationship. The field homogeneity is attained by the magnet construction improvement, thermostating of the yoke, shimming with auxiliary coils. The sample spinning gives a considerable improvement in resolution too. Resonance condition stabilization methods known at present are less satisfactory because they do not correspond in precision to the minimum line width.

In the spectrometers in which the field-frequency relationship is maintained by the independent stabilization of both quantities, a good long time stability can not be attained at all. Better performance reveal the spectrometers in which nuclear magnetic resonance of the second auxiliary sample is used. In this way the possibility arises of maintaining the field-frequency relationship without seeking the high grade stability of both quantities separately. For this purpose the automatic frequency control [1], proton stabilizer [2, 3], super-regenerator in a coherent mode of operation [4] are used. In Varian A-60 spectrometer a version of « spin generator » proposed by Schmelzer [5] is used. In principle, application of the « maser » type apparatus [6] is also possible. The static precision

of all of the above-mentioned stabilizing devices is sufficient for high-resolving spectrometers. It seems that the spin generator is the best rapid-operating device.

It must be mentioned, however, that in two sample spectrometers the high stability is not insured by the very principle of operation. The chemical shift cannot be found directly. The results depend on the difference in field at the two sample sites, on some (unknown) fraction of the control line width, and on the parameters of the sweeping coils. Besides, the above mentioned methods of the field homogenization do give a good uniformity in some near vicinity of one arbitrary chosen point that is in *one* sample only. In two sample spectrometers the control sample would be located in the field with worse homogeneity than that in the sample under study, which diminishes sufficiently the precision of the stabilization. So the use of the separate sample for the stabilization purposes can give the precision of measurements necessary at the present resolution level at the cost of a number of parametric stabilization measures and of some calibrations only. Further improvement of the resolution by using this method of stabilization is hardly possible.

2. We constructed and tested a spectrometer which to a considerable extent is free from the above-mentioned shortages (fig. 1). For the spec-

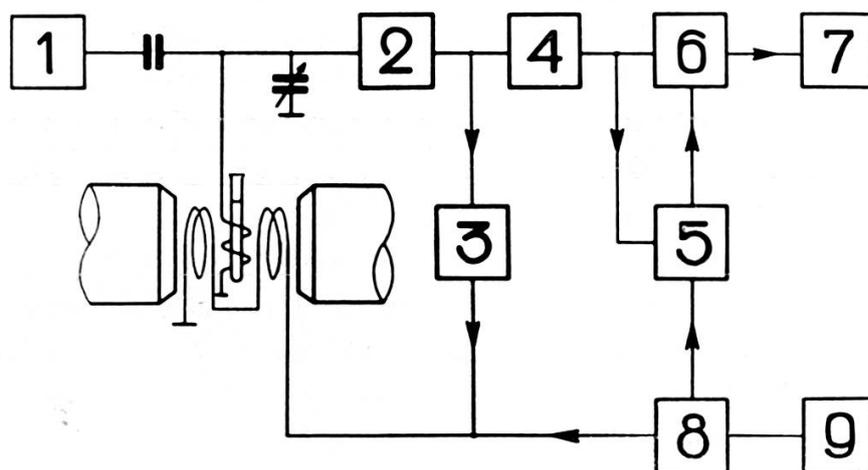


Fig. 1.

Block diagram of the N.M.R. spectrometer.

- 1) *r.f.* oscillator; 2) receiver; 3) limiting amplifier; 4) linear amplifier;
 5) balanced modulator; 6) synchronous detector; 7) recorder; 8) *a.f.* generator;
 9) crystal calibrator.

trum study and for the precise stabilization, a single sample is used¹. The strongest of the lines is the control one and is used for the stabilization by the spin generator method. The rest of the lines are recorded by using a double modulation. The control line can be one of the substance under investigation or of another substance. Tetramethylsilane is the most convenient [7] as its line lies outside most of the spectra.

Our apparatus and circuitry includes few unusual elements. Rollin type detector [8] operating at 36.27 Mc/s is used. Its tuned circuit is loosely coupled to the crystal-controlled r.f. oscillator. The receiver converts the amplitude modulation of the r.f. voltage across the tuned circuit to an audio frequency signal. Oscillation of the spin generator type is excited by the amplified output of the receiver being applied to the modulating coils. The magnetic field H_0 is regulated so that the resonance frequency of the control line is about 2 kc/s higher than that of a r.f. oscillator. The frequency of oscillation is determined by the resonance condition for modulated fields [9]

$$\gamma H_0 = \omega_0 + n\Omega, \quad (1)$$

where γH_0 is the resonance frequency in the d.c. field, ω_0 frequency of the r.f. oscillator, Ω frequency of modulation, and n any integer. In our case $n = 1$ that is the first side band is used. The precision with which the frequency of oscillation fits eq. (1) depends essentially upon the line width. In the most important case of a very small line width the sample characteristics are the main source of the phase changes in the feedback loop and the frequency of oscillation fits eq. (1) very closely. The frequency of oscillation supplements the r.f. oscillator frequency up to the exact resonance value, which makes it possible to use such a self-excited system for the precision stabilization purposes.

The main point in the realization of such a mode of operation of the spin generator is the stability of oscillation controlled by a narrow line, obtained from matter with large value of the relaxation time. Without some special measures the selfexcitement process may proceed to the interrupted oscillation.

In our case a high degree of the oscillation stability is insured by the insertion of a noninertial nonlinearity — of a limiting amplifier — in the

¹ The second sample with a broad line is used in a proton stabilizer [3] for the preliminary stabilization.

feedback loop. High precision in the field strength — frequency control can be obtained without very high parameters of the receiver, amplifier and modulating coils. With the line width of 1 c/s and the amplifier band width of only 1 kc/s, the stabilization ratio will be about 10^3 . Fast action is secured by noninertial change of the magnetic moment precession frequency with the field.

Experimentally, the high precision of the stabilization is confirmed immediately by the constancy of the amplitude of the control signal. As far as precision of the field stabilization permitted, the close fit of the frequency of oscillation to eq. (1) was studied. The most essential approbation of the precision of the control is the very good reproducibility of the spectra obtained (see below). Of some interest are the unsteady modes of operation of the spin generator. Thus, when the amplitude of modulation were increased beyond the stability limits, samples with two strong lines give the oscillation controlled by the two lines in turn. The frequency difference gives immediately the chemical shift between the lines, and the periodicity of two modes depends on the relaxation phenomena in two spin systems.

3. The application of the spin generator for stabilization in our spectrometer is based on the fact that the spin generator operating steadily on single narrow line does it equally well with a total spectrum of narrow lines. In the last case the spin generator oscillates on the frequency of the strongest line and the rest of these do not violate the spin generator operation because the resonance condition [1] for these lines is not fulfilled. To study these lines, it is necessary to make the resonance conditions for the second line too. It is attained by using the double modulation. Besides of the spin generator oscillation, the second modulation frequency Ω_1 equal to the frequency difference between the control line and the other one is applied to the modulating coils. In this way the combination tones $\Omega \pm \Omega_1$ of the double modulation are used to excite the signal of the second line. The same results gives the amplitude modulation of the limiting amplifier output too. The resonance frequency differences are sufficiently stable as the field instability is small enough (about 10^{-6} in our case). It is clear therefore that the modulation frequency Ω_1 can give a very stable scale for the chemical shift measurements.

A synchronous detection of signals is used. The balanced modulator (fig. 1) gives the reference signal with the frequencies $\Omega \pm \Omega_1$ and at the same time removes the zero displacement due to the control signal. The

d.c. signal at the output of the synchronous detector is recorded in the usual way. The nonlinear effects, possible in the spin generator and in receiving circuitry, are small when the control signal is strong enough and do not prevent the precise chemical shift measurements.

When recording the spectrum the modulation frequency is swept slowly. The frequency marks are made with the use of a crystal calibrator which permits the direct evaluation of the chemical shift in c/s. Because the control line width is small, the stabilization error is also small, and the values obtained in this way are very close to the chemical shift of the lines against the control one. The maximum precision can be obtained by the usual internal standard method.

As an example, figure 2 shows the recording of the methyl group line

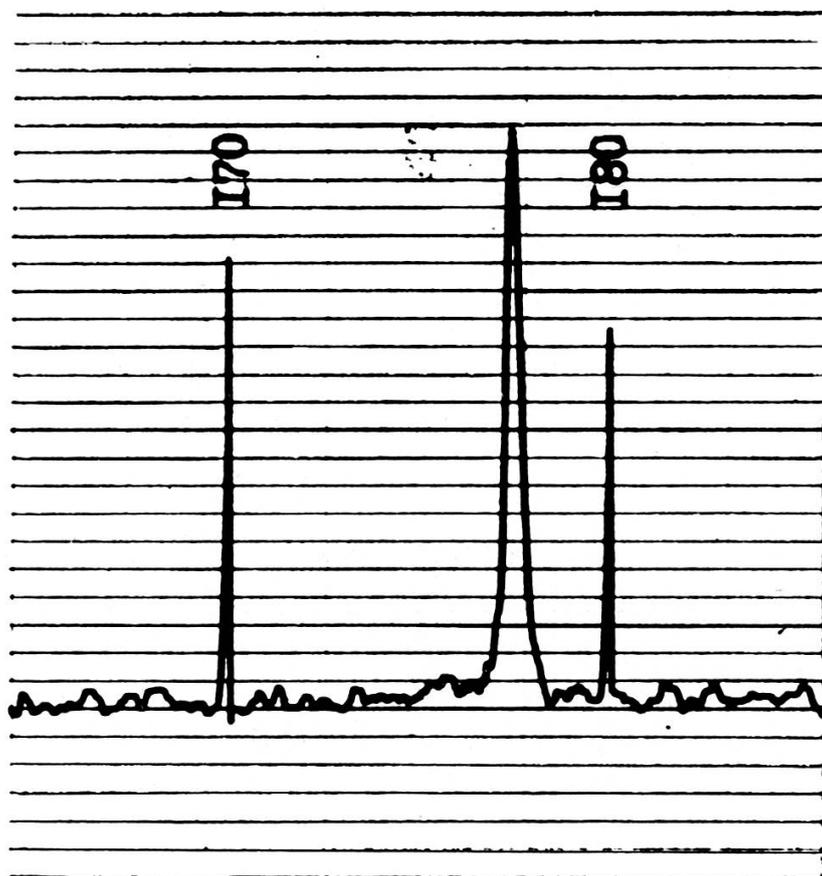


Fig. 2.

Methyl group line in toluene. Frequency marks in c/s.

in toluene. Phenyl group line was used as the control one. The reproducibility of such recordings is very high, better than 10^{-8} .

So far, the single sample stabilization method gives very promising results with the apparatus not specially built and very far from being perfect. High stability of the spectrometer and the presence of the control signal at the output of the receiver do improve essentially the resolution practically realised, as for the best results it is enough to adjust for the maximum control signal strength. To estimate the perspectives, it is important that the precision of the stabilization obtained grows up with the resolution. It seems probable that in the future this will give a possibility to attain the resolution exceeding the so far accesible 10^{-8} .

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DISCUSSION

A. Losche. — Can measurements be made with a large relative change of modulation frequency?

K. V. Vladimirsky. — This is obviously one of shortages. It may be minimized by a special choice of the substance giving the control line.